

ADVANCED HYDROGEN ELECTRODE FOR HYDROGEN-BROMINE BATTERY

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Binary platinum alloys are being developed as hydrogen electrocatalysts for use in a hydrogen-bromine battery system. These alloys have been varied in terms of alloy component mole ratio and heat-treatment temperature. Electrocatalyst evaluation, performed in the absence and presence of bromide ion, includes floating half-cell polarization studies, electrochemical surface area measurements, X-ray diffraction analysis, SEM analysis and corrosion measurements. Results obtained to date indicate a platinum-rich alloy has the best tolerance to bromide ion poisoning.

INTRODUCTION

The hydrogen-bromine battery is being developed by NASA as a power source suitable for space applications. This battery could also be used on earth for large-scale energy storage in load-leveling applications [Refs. 1-4]. The system can be independently sized for various energy and power requirements, and reactants and products stored externally to the electrochemical cell. One proposed configuration of this system utilizes a solid polymer electrolyte membrane, such as Nafion, as the cell separator/electrolyte. A schematic drawing of the regenerative hydrogen-bromine system, showing both the charge and discharge modes, is shown in Figure 1.

The hydrogen-bromine cell has several advantages which make it attractive for use: (a) the system has a high electric-to-electric efficiency because of fast electrochemical reaction kinetics of both the hydrogen and bromine electrodes; (b) the same electrochemical cell can be used for both charge and discharge operations which would lower the power/weight requirements for a space-based power source; (c) it can be operated with shallow discharges and can tolerate both overcharge and over-discharge; (d) the use of a solid polymer electrolyte membrane allows a high differential pressure to be obtained in the cell; (e) the cell has a high coulombic efficiency because of low self-discharge rate; and (f) there are no mass transfer limitations in the cell operation because of the high solubility of bromine in the hydrobromic acid electrolyte.

A major concern of this system which must be resolved is the adsorption of bromide ions on the hydrogen electrode which results in poisoning of the electrode. This problem is caused by the marginal rejection properties of bromine species by presently available commercial solid polymer electrolyte membranes.

Nafion^R-type* membranes which are utilized as perselective solid polymer electrolytes, would ideally transport only protons (or cations). Thus, under ideal conditions in a hydrogen-bromine battery, the hydrogen electrocatalyst will only be exposed to gaseous and ionic hydrogen. In reality, Nafion membranes do not completely prevent bromide ions from migrating across the membrane and adsorbing on the hydrogen electrode. Similarly, the membrane does not completely reject other bromine species

* Nafion^R is a registered trademark of the E.I. duPont Corporation.

(Br₂), which also migrate across the membrane and poison the hydrogen electrode surface. The state-of-the-art hydrogen electrocatalyst, Pt black, is known to adsorb halide ions, "become poisoned," and render decreased hydrogen oxidation/reduction activity [Refs. 5-7]. Studies have shown that this effect can be minimized by always maintaining the electrode at hydrogen potentials. Also, studies conducted in this laboratory under NASA Contract NAS3-24394 have identified a Pt alloy which has improved tolerance to bromine/bromide ion adsorption, as compared to Pt black.

One of the objectives of a current NASA-funded program (NAS3-24878) is the optimization, in terms of stability and performance, of the hydrogen electrocatalyst. This paper describes some of the results obtained during the optimization.

EXPERIMENTAL

The electrocatalyst was prepared by the co-precipitation of platinum and the base metal using a modification of a procedure originally published by Giner, et al. [Ref. 8]. After filtration and drying, the electrocatalyst was separated into smaller batches and subjected to one hour heat-treatment under an inert atmosphere, with heat-treatment temperatures ranging from 500° to 1100°C; platinum to base metal mole ratios were varied from 90:10 to 25:75.

Gas diffusion electrodes were fabricated from the various heat-treated electrocatalysts, using electrocatalyst loadings of 7.5 mg/cm² plus 5% PTFE binder and sintered at 345°C. Carbon fiber paper was used as a substrate. Initial electrodes were fabricated using 20% PTFE. However, these proved to be too hydrophobic for use in the floating half-cell studies. Subsequent to fabrication of a large electrode (typically 20x20 cm), 1 cm² area buttons were cut out and used for either electrochemical surface area analysis by cyclic voltammetry, or floating half-cell polarization studies.

The apparatus shown in Figure 2 was used for the floating half-cell hydrogen oxidation studies; experiments were performed at room temperature, 23 ± 1°C. Initial experiments were run in 2 M H₂SO₄ electrolyte and subsequently in 2 M H₂SO₄ with increasing amounts of bromide ion added in the form of KBr. The data were corrected for iR polarization by a current interruption technique and are presented as over-voltage from the open circuit voltage. The currents were adjusted manually and steady-state potentials recorded.

The effect of bromide ion adsorption on the electrocatalyst surface was studied by measuring the amount of hydrogen adsorbed on the electrode surface using cyclic voltammetry. Electrode potentials were scanned between 50 and 800 mV vs. a dynamic hydrogen electrode, which was located in a separate compartment but in electrical contact with the sensing electrode by means of a Luggin capillary. Results were not corrected for the effect of a liquid junction potential. Electrochemical surface areas were measured initially in 2 M H₂SO₄, and then with increasing amounts of bromide ion added to the solution.

Corrosion testing was also performed on several of the hydrogen electrocatalysts. In this set of experiments, 50 mg of electrocatalyst was placed in 25 ml of 1M KBr/2M H₂SO₄ in a vial containing about 15 ml of air. After 14-20 days at ambient temperature the color of the solutions was noted and the remaining electrocatalyst washed and weighed.

Electrocatalyst powder (no PTFE present) was also examined by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis.

RESULTS AND DISCUSSION

Half-cell polarization curves for hydrogen oxidation on non-heat-treated and 500°C heat-treated G86-1-2 electrocatalysts are shown in Figure 3. For clarity, only the data points obtained in 2 M H_2SO_4 and 4.5 M KBr/2 M H_2SO_4 have been plotted; polarization data was also obtained at intermediate concentrations of KBr.

The results indicate that the heat-treated and non-heat-treated electrocatalysts respond similarly to H_2 in the absence of bromide ion, with the heat-treated sample performing slightly better. However, in the presence of bromide ion, the non-heat-treated catalyst electrode exhibited superior performance. Thus, at 400 mA/cm^2 , the addition of 4.5 M KBr caused a 34 mV additional polarization loss with the heat-treated electrocatalyst, whereas there was only an 8 mV loss with the non-heat-treated electrocatalyst at 600, 800, and 1000 mA/cm^2 . Using the heat-treated electrocatalyst the polarization exceeded 180 mV in the presence of 4.5 M KBr (off-scale on Figure 3), but was less than 140 mV for the non-heat-treated electrocatalyst electrode, even at 1000 mA/cm^2 .

Similar results, not shown, were observed for the G86-1-3 electrocatalyst (lower platinum content), with the lowest polarization losses occurring for the non-heat-treated electrocatalyst, and increasing with heat-treatment temperature. Polarization curves in H_2SO_4 , only for the non-heat-treated G86-1-2 and G86-1-3 electrocatalysts are very similar. However, the additional polarization loss in the presence of bromide ion was larger for the G86-1-3 electrocatalyst system.

Results obtained from the cyclic voltammetry of all five non-heat-treated electrocatalyst systems tested to date are presented in Figure 4. Here we have plotted a normalized response S/S_0 (defined as the ratio of surface area in the presence of bromide ion S , to the surface area in the absence of bromide ion, S_0) as a function of bromide ion concentration. For an electrocatalyst system which was not poisoned by bromide ions, the value of S/S_0 would be unity over the entire range of bromide ion concentrations tested.

It has been demonstrated in the literature that bromide ion adsorption on a smooth platinum surface, for bromide ion concentrations in the range 1×10^{-6} to 1×10^{-3} M will not decrease the area available for hydrogen adsorption [Ref. 6]. These concentrations were not tested here. Instead, bromide ion concentrations from 1×10^{-3} up to 4.5 M were evaluated. In Figure 4, S/S_0 values greater than 1 have been observed for platinum black. It is suspected that during the cycling of the electrode potential the platinum surface is roughened by a dissolution mechanism, thus increasing the effective surface area of the electrode.

The data in Figure 4 suggest that, as the platinum content of the electrocatalyst decreases, the tolerance to bromide ion adsorption also decreases.

A similar plot of S/S_0 was obtained for the G86-1-3 electrocatalyst as a function of heat-treatment temperature. In this set of experiments, plots were obtained for the non-heat-treated, the 500°C and the 700°C heat-treated electrocatalysts. With these results, the best tolerance to bromide ion was found with the non-heat-treated electrocatalyst. Not enough data has been obtained with the other electrocatalyst systems to determine if the trend exists for all systems.

Results of the corrosion test experiments are summarized in Table I. In all cases the non-heat-treated samples dissolved to a much greater extent than the heat-treated samples. Except for the platinum black sample, all the non-heat-treated

samples appear to have liberated bromine in solution, as suggested by the red-to-brown coloration in solution. Heat-treatment, even at 500°C, appears to have changed the stability of the electrocatalyst somewhat, as evidenced by the higher percent recovery of the heat-treated materials. Also, the heat-treated materials do not appear to have liberated bromine as the resulting solutions were either blue or green in color. The most stable materials for a given electrocatalyst system appear to be those heat-treated at 700°C.

The electrocatalyst samples were also examined by means of X-ray diffraction, with results summarized in Table II. X-ray patterns were obtained on electrocatalyst powder directly, using a Norelco X-ray generator type 12045 with a Co radiation source. Lattice parameters, calculated from the position of at least four peaks, are summarized in Table II. Several trends are appearing, but additional data is required. With 500°C heat-treatment, an expansion in lattice parameter was observed. This is not unusual since the size of the base metal is greater than that of platinum. Very little change is noted going from 500 to 900°C, then a drop in parameter occurs with 1100°C heat-treatment. With the non-heat-treated electrocatalyst, a decrease in lattice parameter was noted with a decrease in platinum content.

Finally, scanning electron microscopy was performed on all electrocatalyst samples available at this time. Individual particles were too small to be seen, even at 50 Kx magnification. No significant differences were noted in particle sizes among the non-heat-treated materials. Some sintering was noted with the 900°C heat-treated materials, with a larger amount of sintering occurring with the platinum-rich electrocatalysts.

CONCLUSIONS

Experiments performed previously under NASA Contract NAS3-24394 demonstrated that a non-heat-treated platinum alloy had an improved tolerance to the presence of bromide ion as compared to platinum black. Data obtained to date on the present program and presented here, especially the floating half-cell and cyclic voltammetry results, are also suggesting that a non-heat-treated, or a low-temperature heat-treated platinum-rich electrocatalyst yields the best response and minimum polarization losses in the presence of bromide ion. As demonstrated in Table I, heat-treatment of the platinum alloy improves its resistance to corrosion as evidenced by the higher percent recoveries. Corrosion of the hydrogen electrocatalyst is not expected to be a significant problem, since it can be overcome by maintaining the hydrogen electrode in a hydrogen environment, or, at the very least, by preventing the electrode from reaching an anodic potential where dissolution could occur.

Although it could not be confirmed visually with SEM analysis except for the 900°C heat-treated samples, for a given electrocatalyst composition, the surface area decreased as the heat-treatment temperature increased, due to sintering of the electrocatalyst particles. The larger particle size appears to have less tolerance to the presence of bromide ion, although the reasons for this are unknown at this time. This loss in surface area is also giving rise to increased polarization losses, even in the absence of bromide ion.

Additional information, especially half-cell and cyclic voltammetry is required prior to making a decision as to the composition and heat-treatment conditions of the hydrogen electrocatalyst; these experiments are currently in progress. Also planned are several experiments changing the composition of the base metal alloying component.

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TABLE I

CORROSION TESTING EXPERIMENTS (SOLUTION COLOR AND CATALYST RECOVERY)

Catalyst	Untreated	500°C	Treatment		
			700°C	900°C	1100°C
Pt Black	Lt.Green 64.4%	NT	NT	NT	NT
G86-1-2B	Brown 60.0%	Lt.Green 85.8%	Lt.Blue 90.4%	Lt.Blue 84.8%	Colorless 80.6%
G86-1-3	Reddish- Brown 48.4%	Lt.Blue 91.0%	V.Lt.Blue 92.0%	V.Lt.Blue 88.1%	Colorless 76.0%
G86-1-4	Dk.Brown 69.6%	NT	NT	NT	NT
G86-1-5	Lt.Brown 80.3%	NT	NT	NT	NT

Dk. = Dark
 Lt. = Light
 V.Lt = Very light
 NT = Not Tested

TABLE II

**LATTICE PARAMETERS
CALCULATED FROM X-RAY DIFFRACTION DATA**

Electrocatalyst	Non-Heat-Treated	500°C	700°C	900°C	1100°C
Pt Black	3.911	NT	NT	NT	NT
G86-1-2	3.908	3.915	3.915	3.914	3.908
G86-1-1	3.903	NT	NT	NT	NT
G86-1-3	3.896	3.909	3.908	3.907	3.889

NT = Not Tested

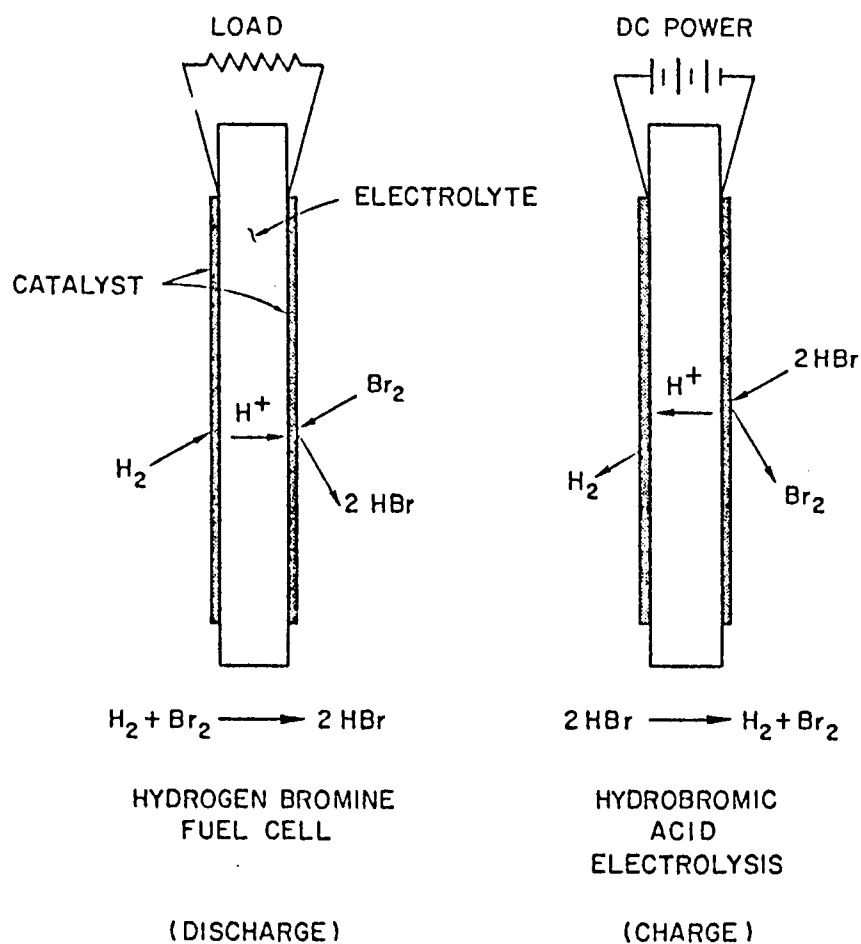


Figure 1: HYDROGEN / BROMINE REGENERATIVE FUEL CELL CYCLE

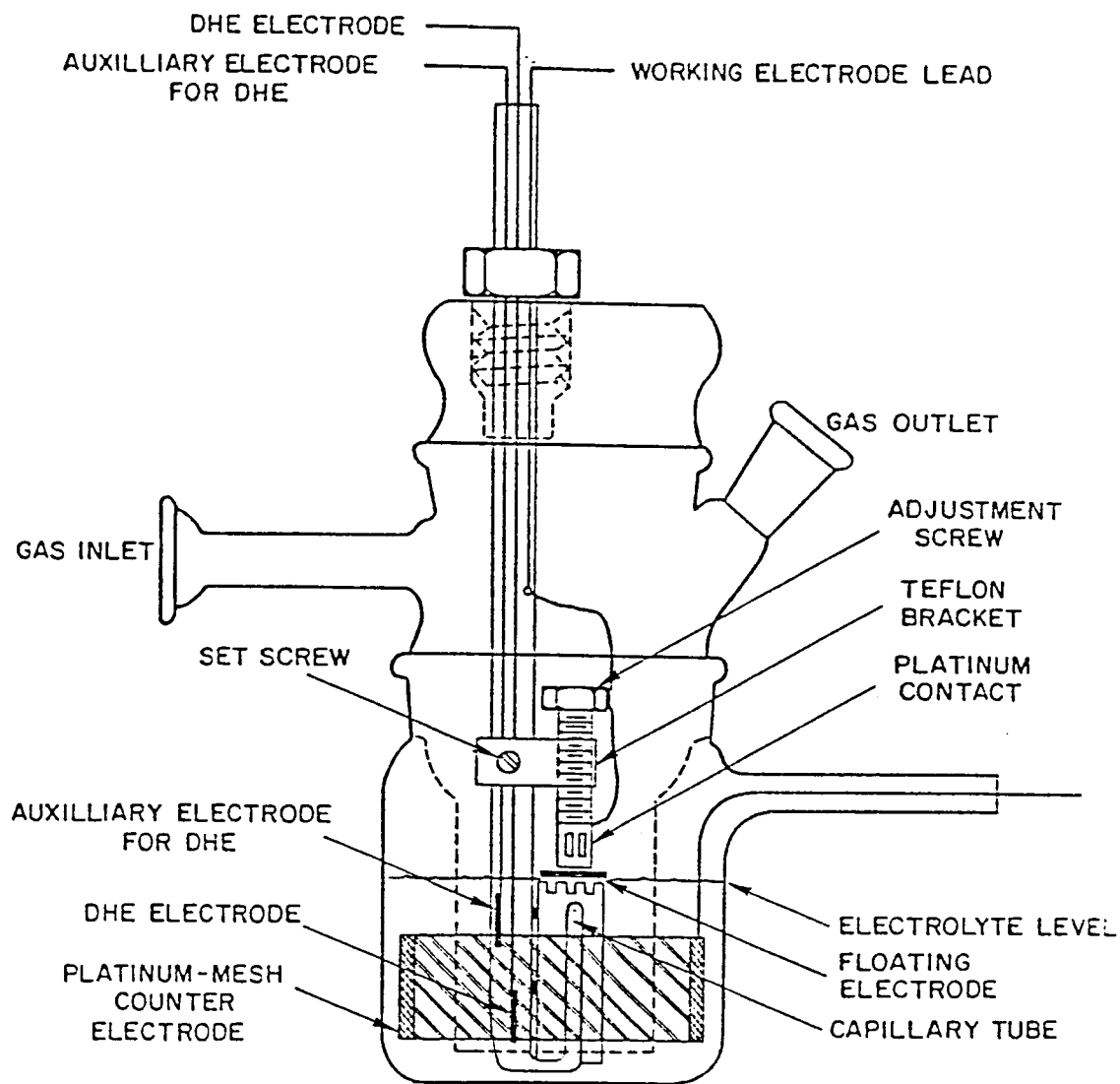


Figure 2: FLOATING ELECTRODE HALF-CELL APPARATUS

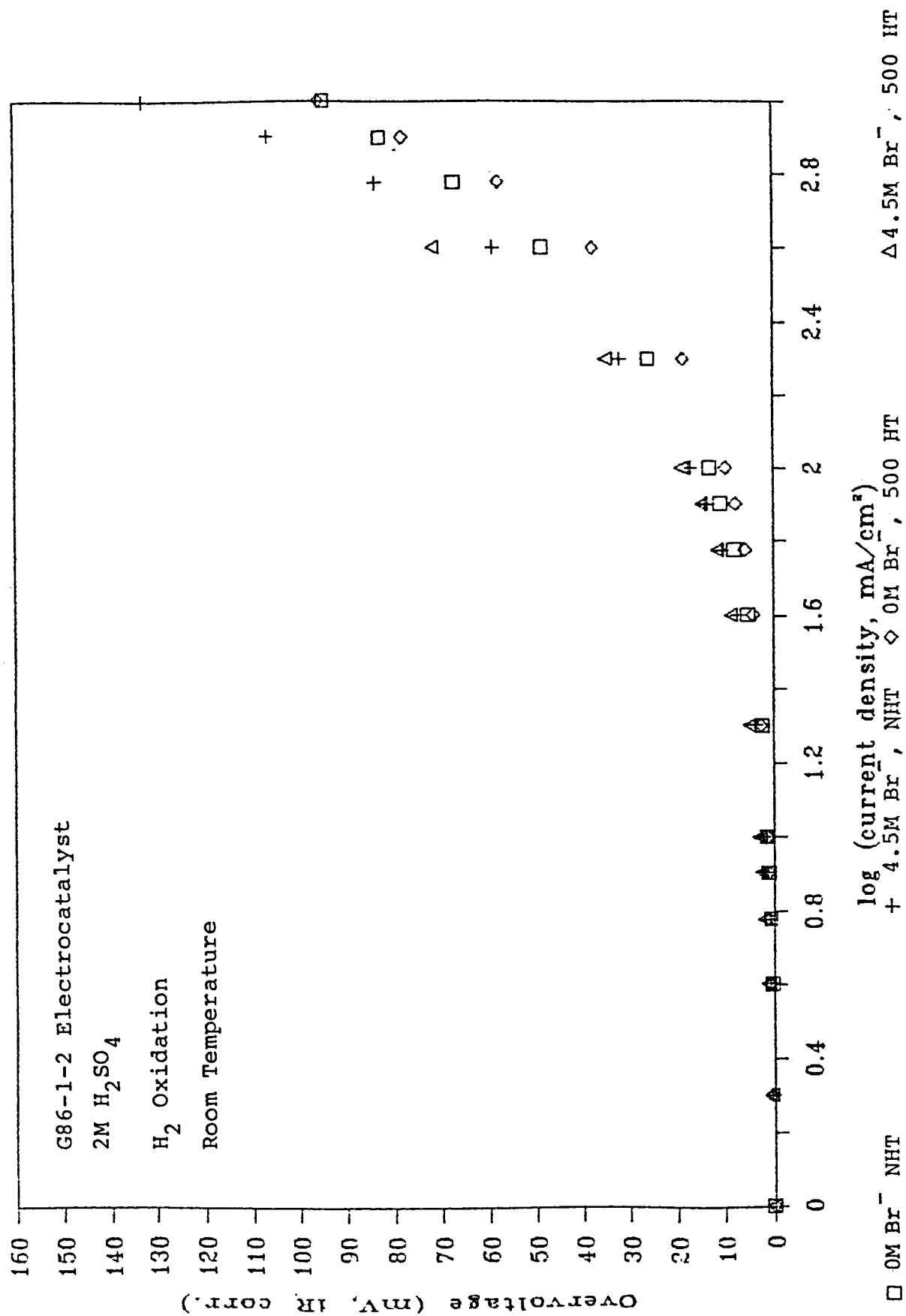


Figure 3: Effect of Bromide Ion and Heat-Treatment Temperature on H₂ Oxidation.

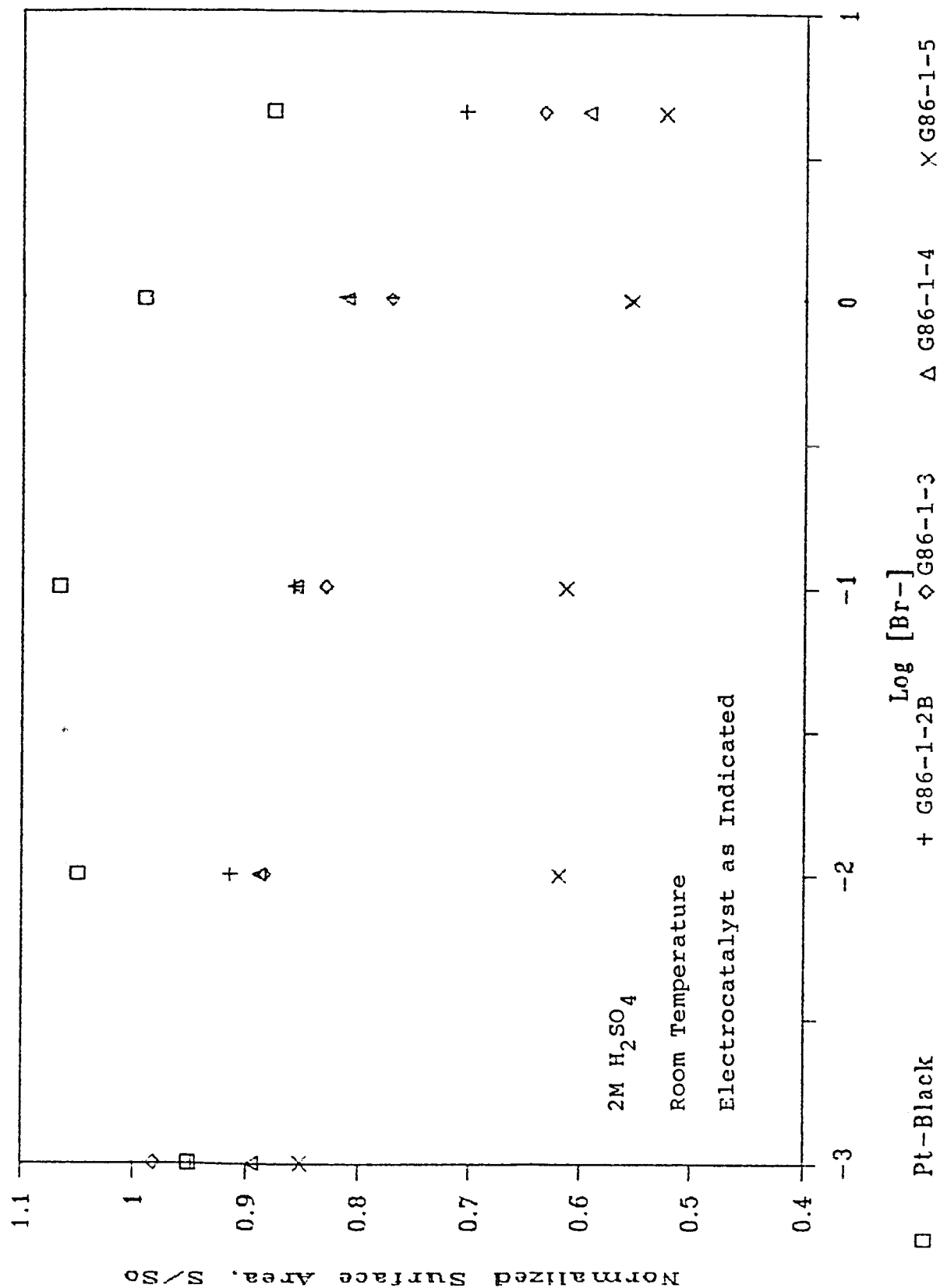


Figure 4: Effect of Bromide Ion Adsorption on Electrocatalyst Surface Area.